

2

AD-A212 225

OFFICE OF NAVAL RESEARCH

Grant N00014-88-K0109

R&T Code 413m005

Technical Report # UMR-FDB-11

Magnetic Resonance of Polymers at Surfaces

by

Frank D. Blum

Department of Chemistry and Materials Research Center  
University of Missouri-Rolla  
Rolla, MO 65401

(314) 341-4451

Prepared for Publication in

Colloids and Surfaces

August 28, 1989

DTIC  
ELECTE  
SEP 12 1989  
S B D

Reproduction in whole, or in part, is permitted for any purpose of the  
United States Government.

This document has been approved for public release and sale: its  
distribution is unlimited.

11 066

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified		1b. RESTRICTIVE MARKINGS										
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for Unlimited Public Release										
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE												
4. PERFORMING ORGANIZATION REPORT NUMBER(S) UMR-FDB -11		5. MONITORING ORGANIZATION REPORT NUMBER(S)										
6a. NAME OF PERFORMING ORGANIZATION University of Missouri-Rolla	6b. OFFICE SYMBOL (if applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research (ONR)										
6c. ADDRESS (City, State, and ZIP Code) Department of Chemistry University of Missouri-Rolla Rolla, MO 65401		7b. ADDRESS (City, State, and ZIP Code) Chemistry Division 800 Quincy Street Arlington, VA 22203										
8a. NAME OF FUNDING/SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (if applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-88-K-0109										
8c. ADDRESS (City, State, and ZIP Code)		10. SOURCE OF FUNDING NUMBERS <table border="1"><tr><td>PROGRAM ELEMENT NO N00014-88</td><td>PROJECT NO. K-0109</td><td>TASK NO.</td><td>WORK UNIT ACCESSION NO</td></tr></table>		PROGRAM ELEMENT NO N00014-88	PROJECT NO. K-0109	TASK NO.	WORK UNIT ACCESSION NO					
PROGRAM ELEMENT NO N00014-88	PROJECT NO. K-0109	TASK NO.	WORK UNIT ACCESSION NO									
11. TITLE (Include Security Classification) Magnetic Resonance of Polymers at Surfaces												
12. PERSONAL AUTHOR(S) Frank L. Blum												
13a. TYPE OF REPORT Interim	13b. TIME COVERED FROM 1/89 TO 8/89	14. DATE OF REPORT (Year, Month, Day) 1989, August 28	15. PAGE COUNT 29									
16. SUPPLEMENTARY NOTATION Colloids and Surfaces, in press												
17. COSATI CODES <table border="1"><tr><td>FIELD</td><td>GROUP</td><td>SUB-GROUP</td></tr><tr><td></td><td></td><td></td></tr><tr><td></td><td></td><td></td></tr></table>	FIELD	GROUP	SUB-GROUP							18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) polymers, surfaces, NMR, molecular motion, FCR		
FIELD	GROUP	SUB-GROUP										
19. ABSTRACT (Continue on reverse if necessary and identify by block number) A brief review of the use of magnetic resonance of polymer molecules attached to solid surfaces is given with examples from the author's laboratory. Liquid, solid (including wide-line and magic angle spinning), and two dimensional magnetic resonance experiments have all been performed on surface polymers. The results suggest how magnetic resonance techniques can be used to probe the dynamics and structure of the polymer in composites, dispersions, surface treatments and the drying of coatings.												
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION Unclassified										
22a. NAME OF RESPONSIBLE INDIVIDUAL Kenneth J. Wynne		22b. TELEPHONE (Include Area Code) 202-696-4409	22c. OFFICE SYMBOL ONR (Chemistry)									

## ABSTRACT

A brief review of the use of magnetic resonance of polymer molecules attached to solid surfaces is given with examples from the author's laboratory. Liquid, solid (including wide-line and magic angle spinning), and two dimensional magnetic resonance experiments have all been performed on surface polymers. The results suggest how magnetic resonance techniques can be used to probe the dynamics and structure of the polymer in composites, dispersions, surface treatments and the drying of coatings.

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	



## INTRODUCTION

In most of the applications where polymers are used, more than one phase is present. In addition to the polymer matrix, the second phase may be comprised of the same or a different polymer, or of some type of filler or fiber which is typically a solid or solid-like. Typical applications of these materials include use in: structural composites; adhesives; chromatography; protective coatings; elastomers; and particle stabilization and separation.

Perhaps the most innovative structural materials to be used in the last 20 years have been composite materials which are used because combinations of existing materials often out perform the homo-materials. The most ubiquitous of these are composites made using a polymer matrix and fibers. The polymeric matrix performs a number of tasks, but its major role is to hold the material together. The fiber gives the material rigidity and often reinforcement. The physical properties of the composite depend on a number of things including not only the properties of both the matrix and the resin, but also the properties of the interfacial layer between the two. In the dispersion, flocculation, or precipitation of particles, the role of the polymer is to change the interaction between the particles. The resulting interaction may be repulsive, so that stabilization is achieved, or attractive, so that coagulation results. There are a variety of ways either of these results can be produced and controlled, such as the nature of the polymer, presence of solvent, etc.

In general, the properties of polymers adsorbed on solid surfaces are difficult to probe directly by most mechanical techniques because the layers are microscopic. Rheological properties and capillary flow can sometimes be sensitive to the surface environment, but microscopic probes, which are often spectroscopic, need to be

employed. These probes are useful because they are sensitive to either the structure or dynamics (sometimes both) on an atomic or molecular scale. Historically, most of the studies of interfacial species have been oriented towards structural properties. Shifts in resonance positions with changes in bonding (primary or hydrogen) from infra-red, magnetic resonance, and electron spectroscopies give direct information on structure. Fewer studies have focussed on molecular mobility, even though the dynamic properties of the interfacial polymers are probably just as important as the structural ones with respect to the physical properties of the systems.

In this paper, the use of magnetic resonance (MR) to probe both the structure and dynamics of polymeric species on solid surfaces will be briefly reviewed and illustrated with examples from the author's laboratory and those of others. Although a wide variety of interfaces are important in polymer technology, the present work will be limited to polymers adsorbed or coated on solid surfaces. No attempt has been made for a complete review of all the literature on the subject, but rather the main points will be demonstrated with illustrative examples.

## BACKGROUND

It is interesting to compare the adsorption of polymers and small molecules on solid surfaces. The primary association between the surface and adsorbed atoms is quite similar for both. Usually, hydrogen bonding, ionic attractions, van der Waals forces or other atomic scale interactions hold the molecules at the surface. These are rather short range (a few to several Ångstroms) and only involve a few atoms. On the other hand, secondary effects are much more important for polymers. Specifically, in adsorbed polymers, polymer segments which are too far away from the surface to be directly influenced by it are indirectly perturbed because of (i) the restriction of the overall motion of the polymer, and (ii) the perturbation of the conformation and dynamics of the polymer. Consequently, the study of polymers on surfaces is more complicated than that of small molecules.

A number of reviews of theoretical and experimental studies of adsorbed polymers exist.<sup>1-7</sup> To describe the conformations of adsorbed polymers, it is convenient to divide the polymers into three major classes: (i) homopolymers and random copolymers, (ii) terminally attached polymers and (iii) block copolymers.<sup>8</sup> Idealized conformations of these are shown in Figure 1. For homopolymers or random copolymers, regions of the adsorbed polymer of different structure and mobility are observed.<sup>2,3,5</sup> Trains are polymers segments directly bonded or very close to the surface. It is expected that these segments would be highly motionally restricted due to interaction with the solid surface. Loops are segments between trains, further away from the solid surface and often more mobile. Tails are the ends of chains which typically are not directly adsorbed and the most mobile polymer segments.

The configuration of terminally attached polymers is somewhat different than

homo- or random copolymers. These polymers can be prepared so they have little affinity for the surface except at the terminal group where they may be bound by chemical reaction or other strong attraction (e.g. ionic) to the solid. As in the previous case, the method of adsorption, temperature, and solvent present can have significant effects on the polymer conformation. The critical factors affecting the structure appear to be the distance between the molecules on the surface and the radius of the polymer molecule.<sup>7</sup> In the limit of isolated chains, expected from dilute solutions, the structure of the polymer on the surface resembles the "mushroom" shown in Figure 1. The "brush" structure is expected for tightly packed chains.

The situation for block copolymers is similar to that for terminally attached polymers provided one of the blocks has a strong affinity for the surface and the other block has little affinity for it. This affinity is considered relative to that of the solvent, in which the colloid will be suspended. The length of the adsorbing segment in block copolymers should dictate the distance between the adsorbed polymers and the length of the non-adsorbing block should control the radius. Thus, synthetic control of the surface structure is possible. However, experimental verification of the surface structure is still far from being definitive.

## EXPERIMENTAL

Since this paper is in part review, only a limited experimental section will be presented. The spectra shown in the figures have been taken on a VXR-200 (Varian Associates) operating at 200, 50 and 31 MHz for protons, carbon-13 and deuterium, respectively. The solid-state carbon-13 spectra were taken using cross-polarization (CP), dipolar decoupling (DD), and magic angle spinning (MAS) with side band suppression (TOSS) and for the plasma polymer proton dephasing (PDP) was used. The 90° pulse width for carbon-13 was about 9  $\mu$ s and the same power used for cross-polarization. About four times this power level was used for dipolar decoupling. Cross-polarization time varied from 0.5 to 2 ms. Magic angle spinning speeds of 3-4 kHz were used. For solids deuterium, the quadrupole echo sequence with a 90° pulse width of about 2  $\mu$ s, a 1.6 MHz spectral width, and phase alternation to reduce acoustic ringing were used. For liquids deuterium a 8  $\mu$ s pulse width was used with the inversion-recovery or Carr-Purcell Meiboom-Gill (CPMG)-T<sub>2</sub> sequence.

## RESULTS AND DISCUSSION

**Composite Materials.** Most of the research on composite materials has been done on rubber (natural and synthetic)-filled composites. These systems are amenable to NMR studies because the polymer is flexible in bulk and can have significantly reduced mobility when adsorbed on solid surfaces. Much of the early work was based on proton NMR and has been reviewed by Douglass and McBrierty.<sup>9</sup> They cite the usefulness of NMR, particularly proton NMR, as being due to the short range nature of the dipolar interaction and its sensitivity to spin energy exchange.

Kaufman *et al.*<sup>10</sup> have found at least two components in the relaxation behavior ( $T_2$ ) of the bound (insoluble) fractions of cis-butadiene and ethylene-propylene-diene rubbers (EDPM) filled with carbon black. The proton  $T_2$ s in both bound rubbers were as much as one and two orders of magnitude shorter for the relatively mobile and immobilized fractions, respectively, than in the bulk polymer.<sup>10</sup> This suggested the long range effect of the surface on the polymer. At about 50 °C above the  $T_g$  (bulk polymer) and lower, all of the components appear to be immobile. The difference between the thermally measured  $T_g$ , and the one to which magnetic resonance is sensitive, is due to the faster motions which affect the relaxation times. Later, studies of carbon black filled rubber were resolved into three components from  $T_2$  measurements.<sup>11</sup> These were assigned to a layer of polymer tightly bound to the particles, a more loosely bound rubber, and the bulk phase of rubber. From the amounts of material available, the total thickness of the bound layer corresponds to about 6.6 nm with the tightly bound layers corresponding to about 1.4 nm.<sup>9,11</sup>

Proton experiments on silica-filled polyisoprene and polybutadiene have verified the above multicomponent relaxation, however, the dependence on

processing conditions of each is different.<sup>12</sup> Multiple pulse NMR has also been used to determine the contributions to the observed proton lineshapes from the polymer.<sup>13</sup> The major components contributing to the breadth of the resonance for filled, vulcanized and natural rubber were found to be from chemical shift and dipolar effects. Spin-spin relaxation rates were found to be an order of magnitude faster for the filled sample.<sup>13</sup> More recently, MAS experiments (with high power decoupling used during detection) have been used to obtain <sup>13</sup>C J-resolved two-dimensional spectra of bulk rubber.<sup>14</sup> The couplings in this case are found to be the same as those in the solution spectra of the polymer. In carbon black filled natural rubber, the <sup>13</sup>C linewidths are found to be 5-10 times larger than in the bulk polymer. The filler, carbon black, was determined to broaden the resonances due to susceptibility effects and also to restrict of the motion of most segments so that residual dipolar couplings are still present.<sup>14</sup> Similar effects have been observed due to chain entanglements or crosslinks.<sup>15,16</sup> Further experiments on polydimethylsiloxane (PDMS)-silica systems have verified the similarity between the attachment of the chains to silica particles and the chain entanglements in polymer melts.<sup>17,18</sup> The distribution functions describing the chains, connecting either entanglements or particles, and the networks themselves, are similar. The addition of silica lowers the mesh size of the system and can be considered as an "affine deformation" of the siloxane system.<sup>17</sup> The silica-siloxane systems with unattached chains removed also have proton T<sub>1</sub> values which are not a function of the silica loadings or reversible solvent swelling beyond a critical value.<sup>18</sup> Thus, these systems behave rather differently than cross-linked gel systems.

There have been a few studies of the use of NMR in more solid-like composites. Veeman *et al.*<sup>19</sup> have used solid-state <sup>13</sup>C NMR to show that the relative amounts of two different crystal structures of polyamide 6 (nylon 6) are affected by filler loadings. Increased amounts of glass microspheres produced more of the  $\gamma$ -form which was converted to the  $\alpha$ -form with time. This suggests the presence of both the long range

surface effects as well as the importance of the consideration of the surface in the processing of composites. Further studies have shown the dependence of the structures formed on processing conditions, initial polymer structure and reaction with surface agents.<sup>20</sup> In the latter, reaction of the polymer with the amine group of  $\gamma$ -aminopropylsilane was suggested as the reason for an increased amorphous fraction in the presence of the coupling agent.

In our own laboratory, we have used both  $^2\text{H}$  and  $^{13}\text{C}$  NMR to observe surface bound polymers. Shown in Figure 2 is the  $^2\text{H}$  NMR spectrum of poly(vinyl acetate)-d<sub>3</sub> in bulk and adsorbed to monolayer coverage on Cab-O-Sil silica. This polymer was labelled in the methyl positions. Since this polymer is below its  $T_g$  at room temperature, the spectrum from the bulk polymer is consistent with a methyl group undergoing fast rotation about its symmetry axis. The spectrum of the surface-bound polymer is also consistent with this as the presence of the surface does not significantly perturb the motion in this glassy polymer. The major difference, however, is in the signal to noise ratios of the two spectra. Even though 32 times as many scans were taken for the surface-bound polymer, worse signal to noise was obtained. This is chiefly due to the dilution of the polymer deuterons by the silica and is representative of a major obstacle in surface NMR.

We have also studied the behavior of poly(isopropyl acrylate) (PIPA) on Cab-O-Sil silica.<sup>21,22</sup> In this system, the solid state carbon-13 spectrum of the surface bound species has better resolution and signal to noise than that of the bulk polymer for several resonances in spite of the dilution effect. This is shown in Figure 3 where the solution spectrum in chloroform is also shown along with the peak assignments. Only the carbonyl and methyl resonances are well resolved in the bulk polymer. The spectrum of the surface bound polymer shows the presence of all of the resonances. In this case the differences in the two spectra are due to the differences in mobility of

the two species. The bulk polymer at room temperature is above the  $T_g$  for PIPA. There appears to be enough mobility in the bulk polymer to either undo the effects of magic angle spinning<sup>23</sup> or the dipolar decoupling.<sup>24</sup> Studies performed with variable contact times suggest that cross-polarization efficiency or proton decay is not the dominant cause of the missing resonances. When adsorbed on the surface, the mobility of the polymer is reduced and probably similar to a glassy polymer so that the spectrum is much like that of a typical glassy polymer such as poly(methyl methacrylate).<sup>22</sup> In addition, decreasing resolution is found with increasing coverage,<sup>22</sup> suggesting a gradient in molecular motion away from the solid surface.

In general the ESR technique is much more sensitive than NMR. This is because of the larger magnetogyric ratio (about 400 times that of a proton) of the electron. To introduce the unpaired electron, polymer samples must be labelled with stable free-radical groups. With as little as 1 out of 10,000 mers labelled, a good quality spectrum of a surface bound polymer can be made with one scan. These labels are sometimes considered to perturb the mobility of the polymer, but it has been shown that both NMR and ESR are similar in their response to solvent and temperature in bulk poly(vinyl acetate) (PVAc).<sup>25</sup> This technique has been used for comparison with bulk polymer for the PVAc-silica and polystyrene (PS)-silica systems.<sup>26</sup> As a function of temperature, comparison of the surface labelled polymer with the bulk polymer reveals that below  $T_g$  little difference between the two is found, whereas above  $T_g$  the surface bound polymers show reduced mobility. As the coverage was increased, the ESR spectra of the polymer also became more bulk-like. The mobility of the PVAc on silica was also shown to depend on the solvent that the polymer was adsorbed from. Finally, it was shown that if a labelled sample on the surface was overcoated with unlabelled polymer, molded, and heated, the labelled material was rapidly exchanged from the surface.

**Dispersions.** One of the major uses of magnetic resonance of polymers on surfaces is to determine the conformation of adsorbed polymers at the solid-liquid interface. Among the earliest studies was by Miyamoto and Cantow<sup>27</sup> who studied the adsorption of poly(methyl methacrylate) (PMMA) on silica gel in deuteriochloroform. They demonstrated that at low coverages, the polymer was held strongly enough at the surface that a high resolution signal from the polymer could not be observed. Isotactic PMMA also appeared to be more restricted on the surface than syndiotactic PMMA.

A number of ESR studies have also been applied to polymers at the solid-liquid interface.<sup>26,28-31</sup> ESR has the additional advantage that analysis of the solution can be used to determine the adsorption isotherm as well as the dynamics.<sup>29-33</sup> Miller *et al.*<sup>26,28</sup> have demonstrated how the dynamics of the adsorbed layer depend on the solvent present, amount of polymer deposited, and the type of surface used. Typically a two component line shape is found in randomly labelled polymers which can be deconvoluted into a mobile and immobile component. These are associated with loops (and tails) and trains, respectively. Considerable effort has been placed on estimating the amounts of polymer segments in loops, trains, and tails in several studies. In general, ESR has given higher estimates in bound fractions than techniques such as IR.<sup>31</sup> This is because ESR (as well as NMR), is sensitive to the mobility of the segment, while IR will only be sensitive to those moieties directly attached. The mobility of segments near, but not necessarily directly attached to the surface (such as those in short loops), is reduced compared to that further away from the surface. These will be counted as bound in the MR experiments. The results from IR, microcalorimetry, NMR and ESR have been compared,<sup>6</sup> and in the latter three, found to be in general agreement for poly(vinyl pyridine) (PVP)/silica/water system.

Grafted poly(ethylene glycol) has been studied by both ESR<sup>32,33</sup> and NMR<sup>34</sup> ESR studies have shown that the segmental mobility as a function of molecular weight

was consistent with a brush model for oligomers and "overlapping partially collapsed chains for polymers". Carbon and proton NMR relaxation measurements indicate multicomponent behavior. The less mobile fraction shows highly anisotropic motion, with the slow mode perpendicular to the surface.

A novel NMR approach was pioneered by Cosgrove *et al.*<sup>35,36</sup> employing both a solid and liquid echo train. The principle is based on the fact that the strongly dipolar coupled spins could be refocussed with a solid echo pulse sequence. Extrapolating this magnetization to time zero provides a measurement of the total number of spins. At later times, a conventional spin echo can be used to estimate the intensity of the mobile spins. In this way a profile of the bound and mobile polymer segments could be estimated. This method also has the advantage of not depending on the deconvolution of lineshapes. This was initially applied to PVP/silica/water and PS/PhilblackO/CCl<sub>4</sub>. Estimates of the bound fraction decreased with increasing surface coverage for both. For comparison, one of the PS samples was terminally attached to the surface and showed no segments in trains. These techniques have also been extended to use in other systems.<sup>37,38</sup>

One of the advantages of specifically tailored polymers is that certain groups can be labelled with an isotope to probe only part of a molecule. This approach has been used in the case of block copolymers of polystyrene co-2-vinyl pyridine (STY-VP) adsorbed on silica. These polymers are produced by sequential addition of monomer in an anionic polymerization.<sup>39</sup> In this case, the styrene segments have little affinity for the silica surface, while the vinyl pyridine strongly adsorbs. Shown in Figure 4 are the <sup>13</sup>C NMR spectra of a VP-STY copolymer, adsorbed on silica, and then swollen with toluene, and the second spectrum is of the polymer in toluene solution. Toluene is a thermodynamically good solvent for the STY polymer, but a poor one for the VP polymer. The spectra show that in the surface bound polymer, the

resonances for the VP are not resolved, while those of the STY are. This is interpreted as due to the VP segments being held rigidly to the silica surface and the STY segments extending in to the solution. In this case the VP segments do not exhibit a "liquid-like" spectrum and the STY does.

In order to probe the dynamics along the chain, we have specifically deuterated half of the STY segments on the methine carbon to produce two polymers, poly(vinyl pyridine-deuterostyrene-styrene (VPDSS) and poly(vinyl pyridine-styrene-deuterostyrene (VPSDS),<sup>40</sup> where the D designates the position of the deuteron. For example, the VPDSS has the deuterated styrene segments in the middle of the chain, next to the VP. These were made by anionic polymerization with sequential addition of monomer for a polymer of 25% VP and 75% STY (or simply S) with weight average molecular weights of about 20,000 g/mol. In each case half of the styrene was deuterated. Specific deuteration on the methine carbon allows the behavior of the styrene backbone to be probed for one C-D species.

In Figure 5, the relaxation behavior of high molecular weight deuteropolystyrene in toluene is plotted as a function of concentration at room temperature. The polymer was adsorbed at a monolayer coverage of about 1.9 mg polymer/m<sup>2</sup> of silica. The deuterated polymers adsorbed on the surface show liquid-like behavior when swollen with toluene. Both the relaxation time measurements showed a single exponential decay within experimental uncertainty. Shown in dashed lines on the figure is the T<sub>1</sub> behavior of the two polymers (VPDSS and VPSDS) adsorbed on silica and swollen with toluene. The T<sub>1</sub> and T<sub>2</sub> for the adsorbed, swollen VPDSS were 3.63 and 3.38 ms, respectively. Those for VPSDS were 3.94 and 3.60, respectively. The experimental uncertainty was less than 5% for these measurements. First, it is noted that the relaxation time values for the bound, swollen VPDSS and VPSDS are not very different. Second, the relaxation time values for either of the polymers (T<sub>1</sub> and T<sub>2</sub>) are

not very different for a given polymer. In fact, they are closer together than in the high molecular weight deuterated polymer (Figure 5). This unexpected result suggests that the motion is more isotropic than the solution polymer. This may be because the conformation of the surface bound polymer (highly extended) is significantly different than that in solution (random coil). The different dynamics reflects itself in rather different relaxation times. Alternatively, the adsorbed polymer's styrene segments are short enough that the tight binding of the VP segments could exclude some of the long range motions that exist in the polymer in solution. These would contribute to the zero-frequency term in the spectral density resulting in a longer  $T_2$  for the surface species. The longer range modes might be present in solution because the VP groups could be involved.

Since  $T_1$  is dominated by shorter range (faster) motions, it is reasonable that this measurement would be less affected by the presence of the surface than by the local concentration. Consequently, the  $T_1$  values were used to estimate the local concentration by comparison to the solution data (Figure 5). The results indicate that the polymer concentration of styrene segments near the bound VP groups is about 11% polymer. Towards the end of the molecule the concentration is lower (4.8%). A rough estimate of the thickness of the styrene layer would then be about 165 Å. This is about four times the radius of gyration expected in dilute solution, confirming earlier results suggesting highly extended styrene chains on mica surface for the same polymers.<sup>39</sup> Further studies with labelled copolymers of varying molecular weight will have to be done to confirm the apparent isotropic behavior of the styrene segments.

**Surface Treatments** There are a variety of surface treatments which have been used to modify the interface between solid substrates and polymers. One of the most promising has been the use of plasmas to produce a modified polymer layer.<sup>41</sup> Unfortunately, since these materials have a complex structure, are highly crosslinked,

and produced as thin tenacious films, they are inherently difficult to characterize.

Definitive work on the structure of plasma polymerized materials has been done by Wilks and Kaplan.<sup>42-45</sup> Initial studies concentrated on the quantization of different chemical species produced by injecting ethane, ethylene and acetylene into rf plasmas.<sup>42,43</sup> Normal CP-MAS spectra show distinct separation into  $sp^2$  and  $sp^3$  hybridized carbon resonances. While to the NMR spectroscopist this separation seems trivial, it is a significant improvement when compared to electron spectroscopy for chemical analysis (ESCA). Further deconvolution suggests the presence of methyl, tertiary and quaternary aliphatic and double bonded carbons. Further studies have used labelled (carbon-13) precursors to determine the reaction pathways taken.<sup>44</sup> These techniques have also been applied to fluorocarbon polymers.<sup>45</sup>

In a collaborative effort, we have been interested in the characterization of polymers produced in the quest for diamond like films. These are characterized by the presence of quaternary aliphatic carbon atoms. Shown in Figure 6 are two spectra of a plasma polymer produced from ethane. This material was produced by scraping thin films from a substrate every couple of hours until enough polymer was produced for NMR characterization. From the regular CP-MAS-DD spectra, this particular material has more aliphatic intensity (ca. 20-60 ppm) than those typically produced using other monomers. The second spectrum shown has been taken of the same sample using proton dephasing.<sup>46</sup> In this case the signals from non-protonated carbons and highly mobile carbons, such as methyl groups, survive after about 100  $\mu$ s of proton dephasing. This results in a separation of the aliphatic carbon intensity at higher frequency (ca. 40-50 ppm). The aliphatic carbon intensity in this region is believed to be due to the quaternary aliphatic carbons which are "diamond-like". In the aromatic range, the presence of non-protonated "graphite-like" carbons is also apparent. Separate resonances due to the methyl groups (ca. 15 ppm) are also present. Of

course true diamond- or graphite-like carbons would not cross-polarize well because they would be far removed from the protons, but in these polymers the numerous defects usually assures that most of the carbons will at least be partially represented.

**Drying of Coatings.** A slightly different application of NMR to adsorbed polymers is based on the use of NMR solvent self-diffusion coefficients to predict the drying of coatings. The use of self-diffusion coefficients in colloidal systems has been reviewed.<sup>47</sup> In coatings, it is well known that two distinct regions of behavior are found in solvent loss curves. These are volatility and diffusion-controlled regions. We have previously reported the computer simulation of solvent evaporation for polymer-solvent systems.<sup>48</sup> This program simulates drying by dividing the film into several thinner regions whose concentration is controlled by Fick's law of diffusion. At the air-film interface, the solvent is allowed to evaporate. The rate is controlled by the pure solvent evaporation rate and the activity of the solvent modified by the presence of the polymer. The activity is well approximated using the Flory-Huggins theory.<sup>49</sup> The transport between the layers is based on the measured self-diffusion coefficients.<sup>48</sup> An upper limit on the timestep is determined by increasing it until a measurable difference in the predicted result is found. Shown in Figure 7 is a plot of the measured and predicted drying curves for toluene in polystyrene solution at 25 °C based on recent diffusion coefficient measurements<sup>50</sup> as extrapolated using the theory of Vrentas and Duda.<sup>51</sup> The agreement between the two curves is excellent considering that there are no adjustable parameters in the model. The shorter time region is controlled by solvent volatility and is not linear even though on this scale it looks so. The longer time region is diffusion controlled. The inset in Figure 7 shows the fit in the transition region. This technique offers possible predictive approaches to the drying of coatings and should be extendible to multicomponent systems. It also offers the advantage of predicting the concentration profile as the system dries.

## CONCLUSIONS

Magnetic resonance has been shown to be a powerful technique for the study of polymers adsorbed on surfaces. A wide variety of effects and samples can be probed because of the variety of different types of experiments available. NMR is perhaps a more versatile technique, but ESR has a major advantage of being much more sensitive. These techniques have the main advantage that they are usually, but not always, sensitive to molecular mobility. This is in contrast to most other spectroscopic techniques which are more directly interpreted in terms of structure.

## ACKNOWLEDGEMENTS

The author wishes to thank the office of Naval Research for its financial support of the project. The author also thanks R.J. Gambogi, B.R. Sinha, R.B. Funchess, and R.A. Waggoner for their assistance during parts of this work. The poly(vinyl acetate)-d<sub>3</sub> was supplied by Prof. W.G. Miller of the University of Minnesota.

## REFERENCES AND NOTES

1. B. Vincent, *Adv. Colloid Interface Sci.*, **4**, 193 (1974).
2. G.J. Fleer, J.M.H.M. Scheutjens, *Adv. Colloid Interface Sci.*, **16**, 341 (1982).
3. A. Takahashi, M. Kawaguchi, *Adv. Polym. Sci.*, **46**, 1 (1982).
4. D.H. Napper, "Polymeric Stability of Colloidal Dispersions", Academic Press, New York, 1983.
5. M.A. Cohen-Stuart, T. Cosgrove, B. Vincent, *Adv. Colloid Interface Sci.*, **24**, 143 (1986).
6. T. Cosgrove, B. Vincent, in "Fluid Interfacial Phenomena", C.A. Croxon, Ed., Wiley, New York, 1986, p607.
7. P.G. de Gennes, *Adv. Colloid Interface Sci.*, **27**, 189 (1987).
8. Block copolymers can in some cases be considered "terminally attached", but in this article terminally attached refers to attachment at the last monomer unit.
9. D.C. Douglass, V.J. McBrierty, *Polym. Eng. Sci.*, **19**, 1054 (1979).
10. S. Kaufman, W.P. Schlichter, D.D. Davis, *J. Polym. Sci., A2*, **9**, 829 (1971).
11. J. O'Brien, E.M. Cashell, G.E. Wardell, V.J. McBrierty, *Macromolecules*, **9**, 563 (1976).
12. M. Ito, T. Nakamura, K. Tanaka, *J. Appl. Polym. Sci.*, **30**, 3493 (1985).
13. C.R. Dybowski, R.W. Vaughan, *Macromolecules*, **8**, 50 (1975).
14. A.P.M. Kentgens, W.S. Veeman, J. van Bree, *Macromolecules*, **20**, 1234 (1987).
15. A.D. English, C.R. Dybowski, *Macromolecules*, **17**, 446 (1984).
16. J.P. Cohen-Addad, R. Dupeyre, *Macromolecules*, **18**, 1612 (1985).
17. J.P. Cohen-Addad, A. Viallat, *Polymer*, **27**, 1855 (1986).
18. J.P. Cohen-Addad, A. Viallat, P. Huchot, *Macromolecules*, **20**, 2146 (1987).
19. T.L. Weeding, W.S. Veeman, H. Angad Gaur, W.G.B. Huysmans, *Macromolecules*, **21**, 2028 (1988).

20. T.L. Weeding, W.S. Veeman, L.W. Jenneskens, H. Angad Gaur, H.E.C. Schuurs, W.G.B. Huysmans, *Macromolecules*, **22**, 706 (1989).
21. F.D. Blum, R.B. Funchess, W. Meesiri, in "Interfaces in Polymer, Ceramic and Metal Matrix Composites", H. Ishida, ed., Elsvier, New York, 1988, p205.
22. F.D. Blum, R.B. Funchess, W. Meesiri, in "Solid State NMR of Polymers", L. Mathias, ed., Plenum, New York, in Press.
23. Suwelack, W.P. Rothwell, J.S. Waugh, *J. Chem. Phys.*, **73**, 2559, (1980).
24. W.P. Rothwell, J.S. Waugh, *J. Chem. Phys.*, **74**, 2721, (1981).
25. F.D. Blum, J.E. Dickson, W.G. Miller, *J. Polym. Sci., Polym. Phys. Ed.*, **22**, 211 (1984).
26. T.M. Liang, P.N. Dickson, W.G. Miller, in "Polymerization Characterization by NMR and ESR", A.E. Woodward and F.A. Bovey, eds., ACS Symp. Ser., 142, American Chemical Society, Washington, DC, 1980, p1.
27. T. Miyamoto, H.J. Cantow, *Makromol. Chem.*, **162**, 43 (1972).
28. W.G. Miller, W.T. Rudolf, Z. Vekksli, D.L. Coon, C.C. Wu, T.M. Liang, in "Molecular Motion in Polymers by ESR", R.F. Boyer and S.E. Keinath, eds., Harwood Academic, Cooper Starion, NY, 1980.
29. K.K. Fox, I.D. Robb, R. Smith, *JCS, Faraday Trans. I*, **70**, 1186 (1974).
30. A.T. Clark, I.D. Robb, R. Smith, *JCS, Faraday Trans. I*, **72**, 1489 (1976).
31. I.D. Robb, R. Smith, *Polymer*, **18**, 500 (1977).
32. H. Hommel, A.P. Legrand, H. Ballard, E. Papirer, *Polymer Comm.*, **24**, 959 (1983).
33. H. Hommel, A.P. Legrand, J. Lecourtier, J. Desbarres, *Europ. Polym. J.*, **15**, 993 (1979).
34. L. Facchini, A.P. Legrand, *Macromolecules*, **17**, 2405 (1984).
35. K.G. Barnett, T. Cosgrove, B. Vincent, D.S. Sissons, M. Cohen-Stuart, *Macromolecules*, **14**, 1018 (1981).
36. T. Cosgrove, K.G. Barnett, *J. Magn. Reson.*, **43**, 15 (1981).

37. T. Cosgrove, J.W. Fergie-Woods, *Colloids Surf.*, **25**, 91 (1987).
38. T. Cosgrove, K. Ryan, *J. Chem. Soc., Chem. Comm.*, 1424 (1988).
39. G. Hadzioannou, S. Patel, S. Granick, M. Tirrell, *J. Am. Chem. Soc.*, **108**, 2869 (1986).
40. F.D. Blum, B.R. Sinha, F.C. Schawb, to be submitted.
41. H. Yasuda, "Plasma Polymerization", Wiley, 1987.
42. S. Kaplan, A. Dilks, *Thin Solid Films*, **84**, 419 (1981)
43. A. Dilks, S. Kaplan, A. van Laeken, *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 2987 (1981).
44. S. Kaplan, A. Dilks, *J. Polym. Sci., Polym. Chem. Ed.*, **21**, 1819 (1983).
45. S. Kaplan, A. Dilks, *J. Appl. Polym. Sci., Appl. Polym. Symp.*, **38**, 105 (1984).
46. R.J. Gambogi, F.D. Blum, H. Cho, H. Yasuda, in preparation.
47. F.D. Blum, *Spectroscopy*, **1(5)**, 32 (1986).
48. R.A. Waggoner, F.D. Blum, *J. Coat. Tech.*, **61(768)**, 51 (1989).
49. P.J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithica, NY, 1953.
50. S. Pickup, F.D. Blum, *Macromolecules*, in press.
51. J.S. Vrentas, J.L. Duda, *J. Polym. Sci., Polym. Phys. Ed.*, **17**, 1085, (1979).

## FIGURE CAPTIONS

Figure 1. Idealized conformations of polymers adsorbed on a solid surface.

Figure 2. Deuterium NMR spectra of solid poly(vinyl acetate)-d<sub>3</sub> in bulk (upper) and on Cab-O-Sil silica (lower). The number of scans is given in the figure.

Figure 3. Solution (lower) and solid state carbon-13 spectra of poly(isopropyl acrylate) in bulk (upper) and with monolayer coverage on silica surface (middle).

Figure 4. The carbon-13 spectra of VPS copolymer in toluene-d<sub>8</sub> in solution (lower) and on silica (upper).

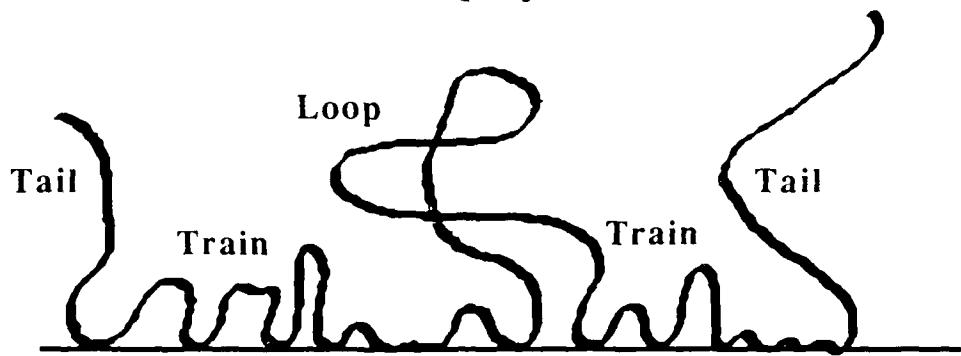
Figure 5. Deuterium NMR relaxation times for deuterostyrene in toluene solution (solid curve) and the T<sub>1</sub>s and extrapolated concentrations for the deuterated copolymers adsorbed on silica swollen in toluene (dashed lines). The VPDSS is at lower T<sub>1</sub> and VPSDS at higher T<sub>1</sub>.

Figure 6. Carbon-13 solid state spectra of plasma produced polymers from ethane. Regular CP-MAS spectrum (lower) and proton dephased spectrum (upper).

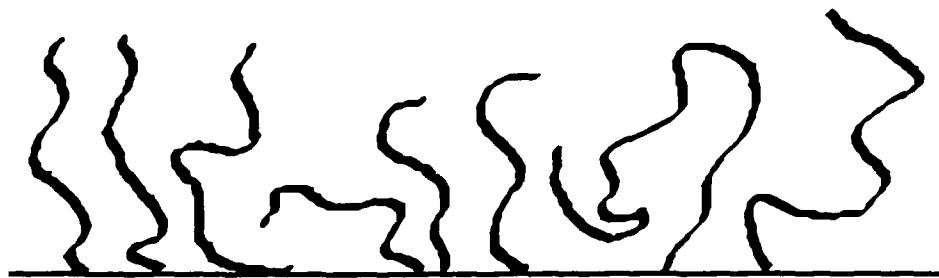
Figure 7. Experimental and theoretical weight loss curves for toluene-polystyrene solution at 25 °C. The inset show the behavior around the transition area which separates the volatility from the diffusion controlled region.

# POLYMERS AT SOLID SURFACES

## Random and Homopolymers



## Terminally Attached Polymers



## Block Copolymers

Brushes

Mushrooms

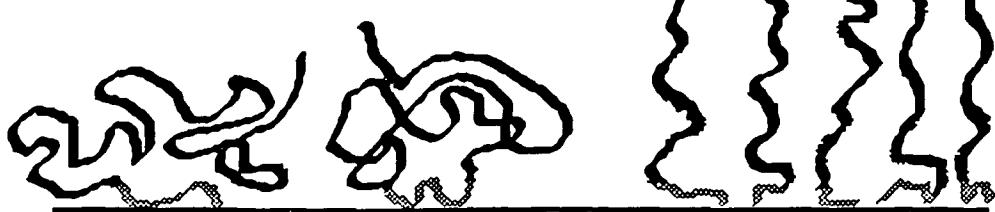


Figure 1. Idealized conformations of polymers adsorbed on a solid surface.

PVAc -  $d_3$

Bulk  
 $NT = 16$

Surface  
 $NT = 512$

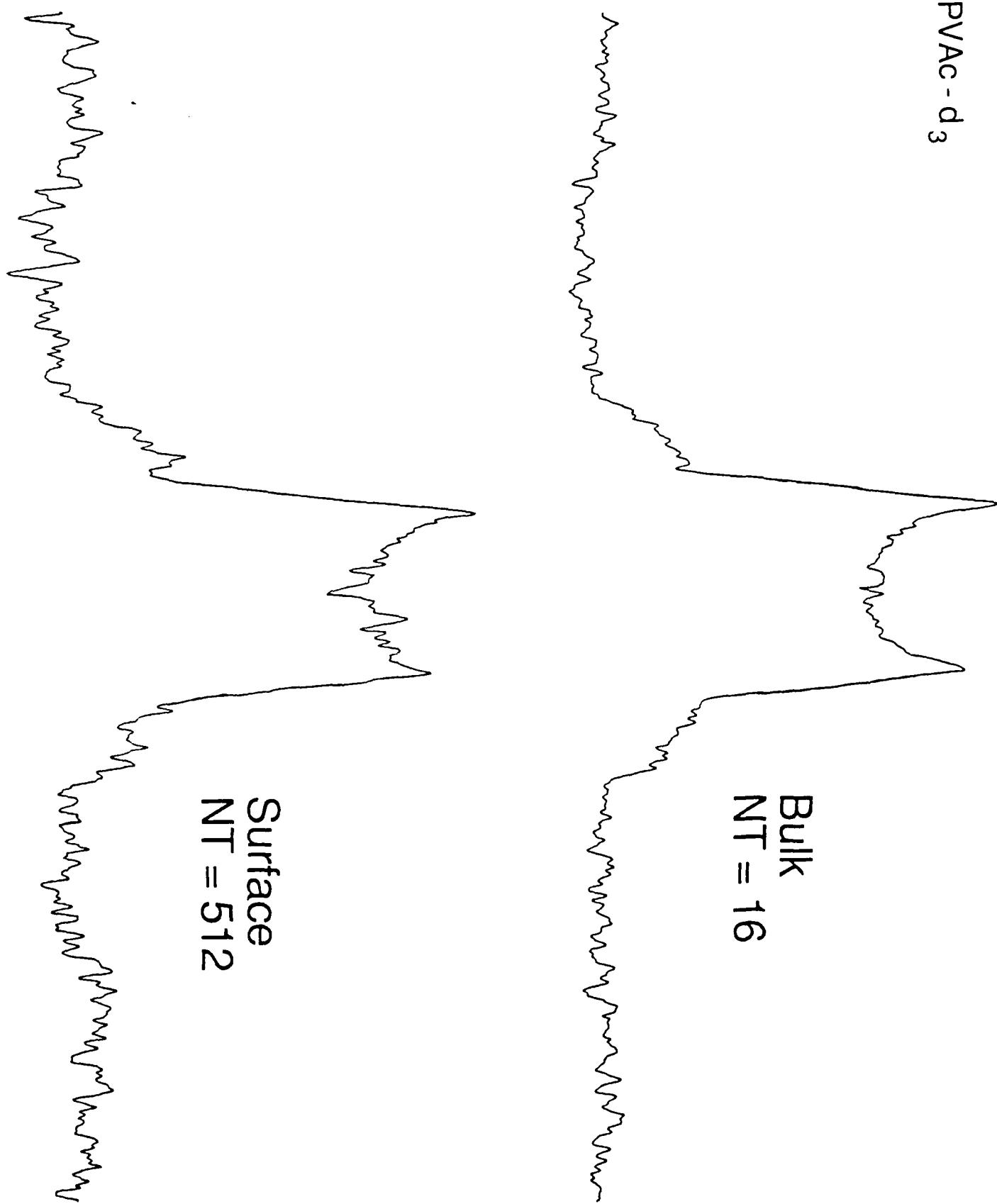


Figure 2. Deuterium NMR spectra of solid poly(vinyl acetate)- $d_3$  in bulk (upper) and on Cab-O-Sil silica (lower). The number of scans is given in the figure.

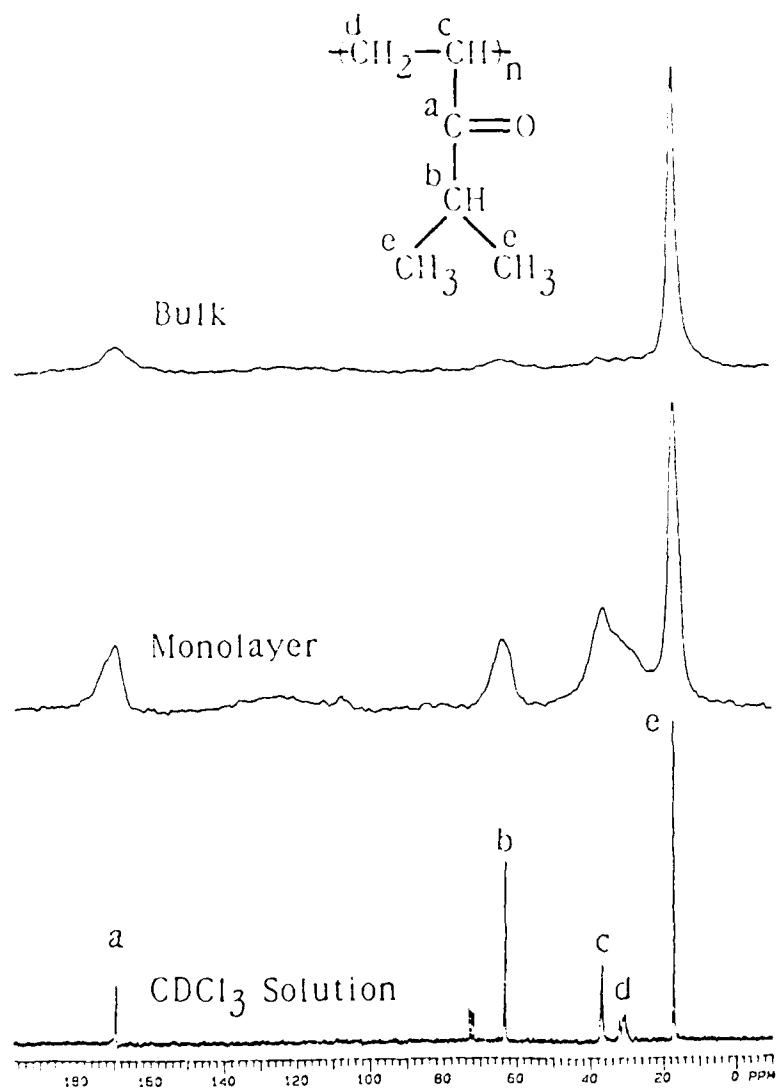
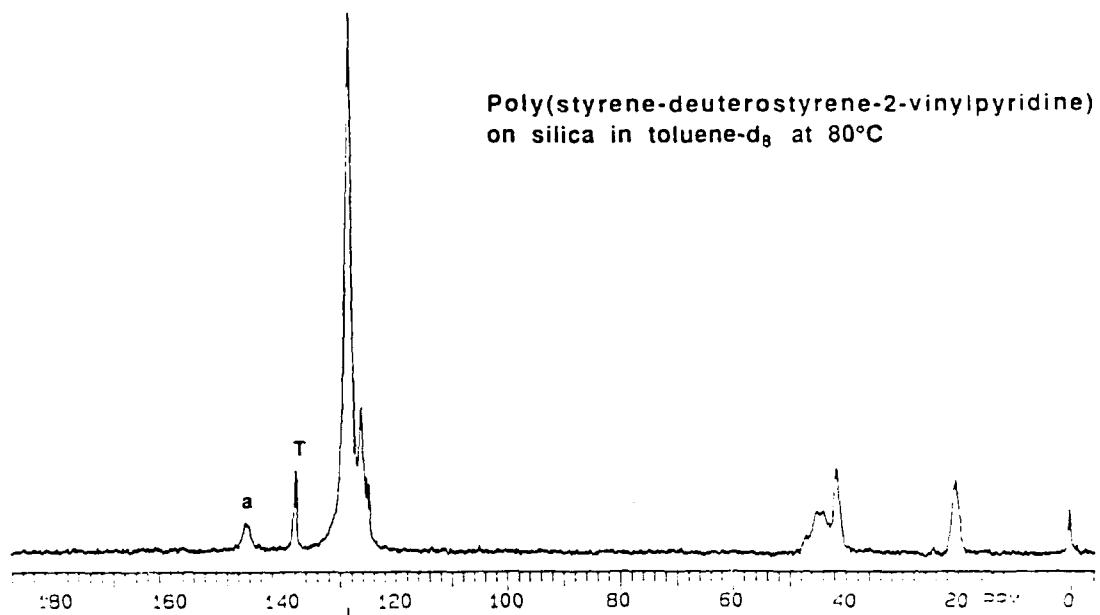


Figure 3. Solution (lower) and solid state carbon-13 spectra of poly(isopropyl acrylate) in bulk (upper) and with monolayer coverage on silica surface (middle).

Poly(styrene-deuterostyrene-2-vinylpyridine)  
on silica in toluene-d<sub>8</sub> at 80°C



Poly(styrene-co-2-vinylpyridine)  
in toluene-d<sub>8</sub> at 80°C

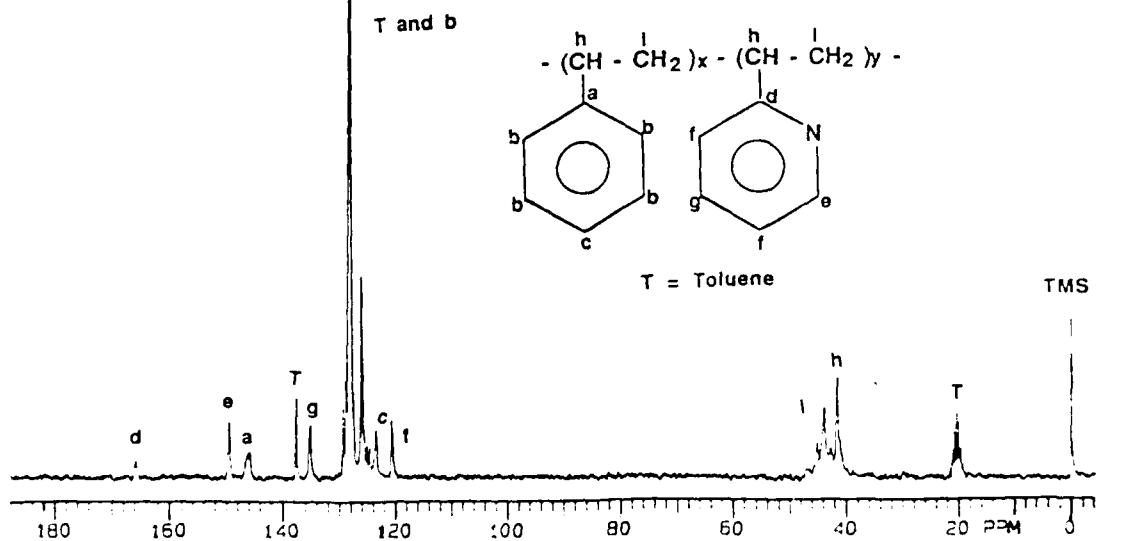


Figure 4. The carbon-13 spectra of VPS copolymer in toluene-d<sub>8</sub> in solution (lower)  
and on silica (upper).

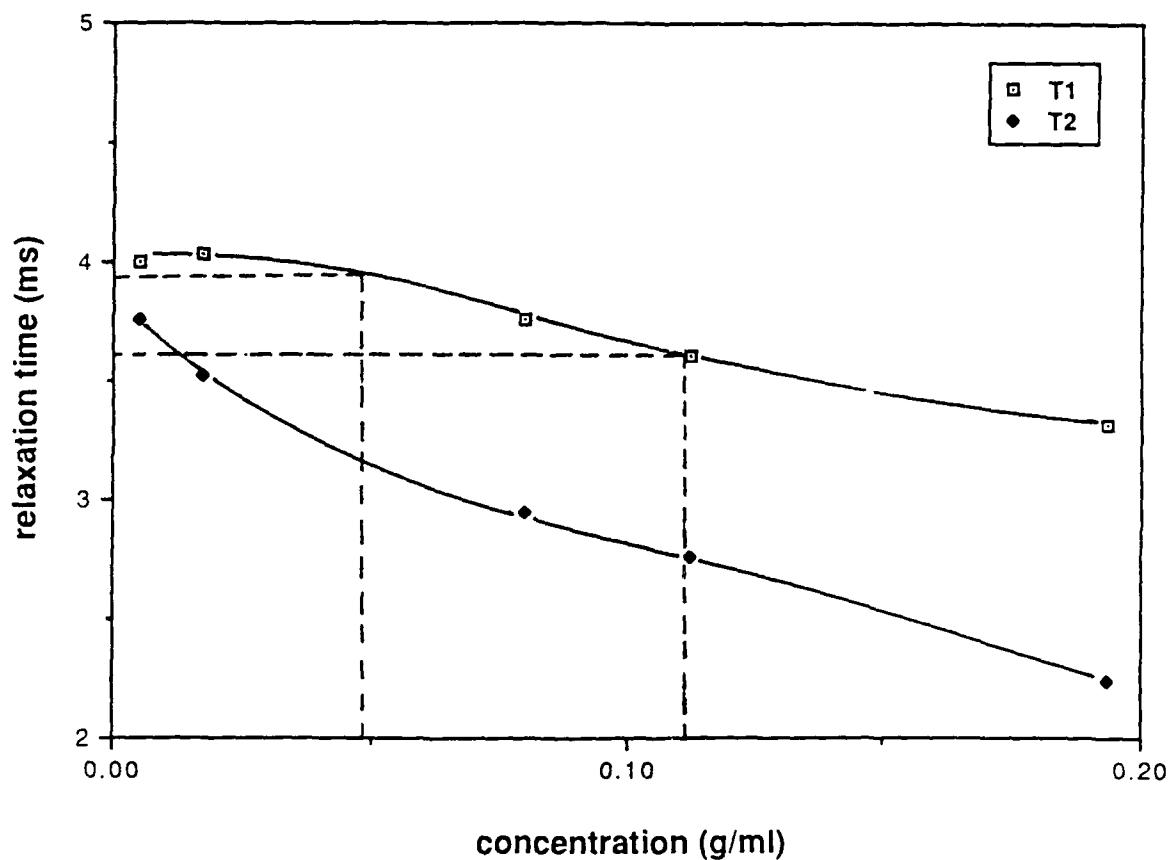


Figure 5. Deuterium NMR relaxation times for deuterostyrene in toluene solution (solid curve) and the  $T_1$ s and extrapolated concentrations for the deuterated copolymers adsorbed on silica swollen in toluene (dashed lines). The VPDSS is at lower  $T_1$  and VPSDS at higher  $T_1$ .

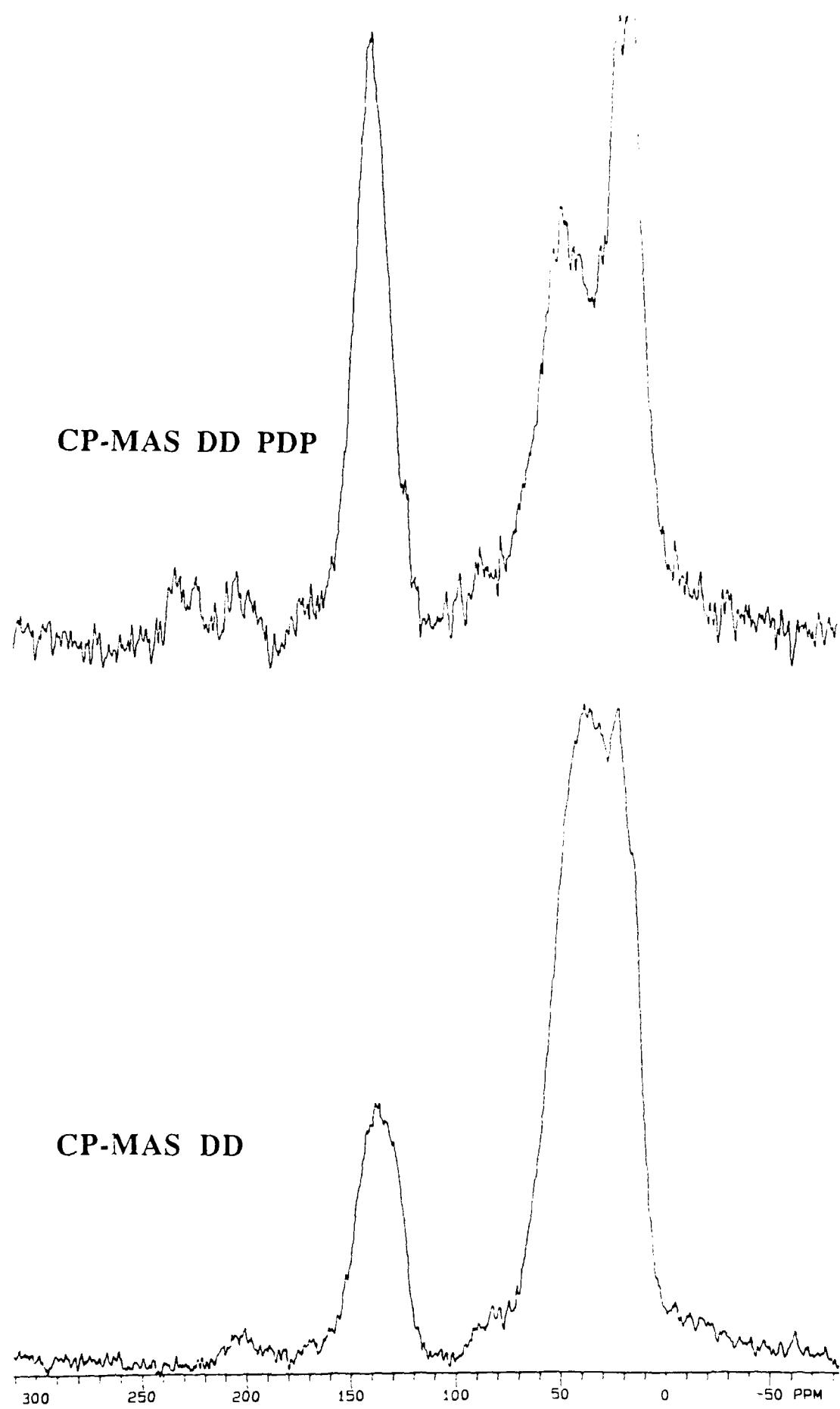


Figure 6. Carbon-13 solid state spectra of plasma produced polymers from ethane.

Regular CP-MAS spectrum (lower) and proton dephased spectrum (upper).

Figure 7. Experimental and theoretical weight loss curves for toluene-polystyrene solution at 25 °C. The inset show the behavior around the transition area which separates the volatility from the diffusion controlled region.

